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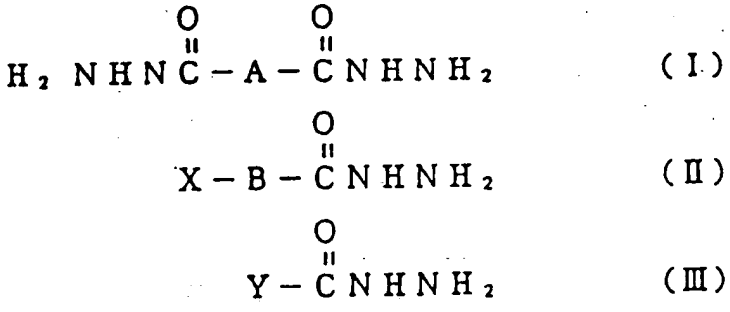
(71) Applicant : **Bridgestone Corporation**
**10-1, Kyobashi 1-Chome Chuo-Ku**
**Tokyo 104 (JP)**

(72) Inventor : **Etoh, Akiko**
**925-10, Araku**
**Iruma-shi, Saitama-ken (JP)**

(74) Representative : **Whalley, Kevin et al**
**MARKS & CLERK 57/60 Lincoln's Inn Fields**
**London WC2A 3LS (GB)**

## (54) Rubber composition.

(57) Heat generation of a rubber composition can be lowered by incorporating into the composition a compound of the formula, (I), (II) or (III),



(I)



(II)



(III)

where A is an aromatic group, hydantoin ring or straight chain hydrocarbon group having up to 18 carbon atoms, B is an aromatic group, X is hydroxy or amino, and Y is pyridyl or hydrazino.

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The present invention relates to a rubber composition of an improved heat generation containing a heat generation improver.

In response to the social demand of resource saving and energy saving, developments of tires of low fuel consumption have been vigorously carried out since several years ago in rubber industry, in particular, tire industry.

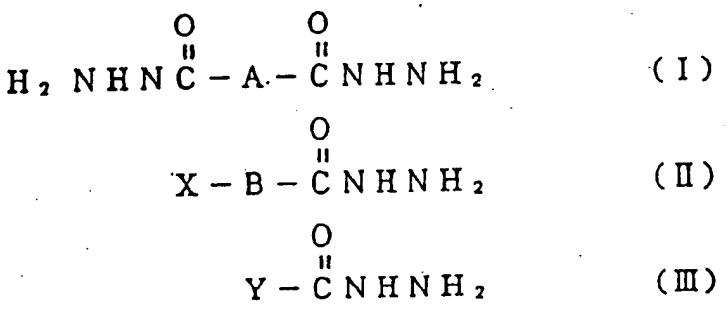
For the development of low fuel consumption tires, low heat generating rubber compositions are indispensable.

Japanese Patent Application Laid-open No. 23409/1985 discloses that styrene-butadiene rubber (SBR) the ends of molecule of which are modified with a particular compound is used for lowering the heat generation, in particular, in the field of tires of passenger cars. This method can be applied to a solution-polymerized SBR, but can not be effectively applicable to other rubbers, in particular, natural rubber widely used for tires of heavy vehicles and emulsion-polymerized SBR having excellent high temperature breaking characteristics.

An object of the present invention is to provide a rubber composition having improved heat generation characteristics.

Another object of the present invention is to provide a rubber heat generation improver applicable to a wide range of field including natural rubber and diene type synthetic rubbers, for example, emulsion-polymerized SBR.

According to the present invention, there is provided a rubber composition which comprises 100 parts by weight of at least one rubber selected from the group consisting of natural rubber and diene type synthetic rubbers, 20 - 150 parts by weight of a reinforcing filler, and 0.05 - 20 parts by weight of a compound selected from the group consisting of the compounds of the formulas (I) - (III),



(I)



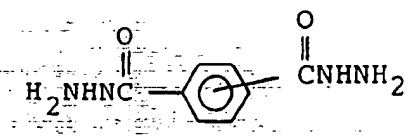
(II)



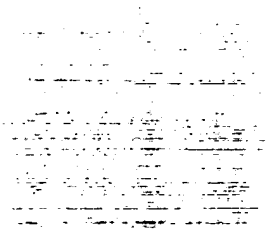
(III)

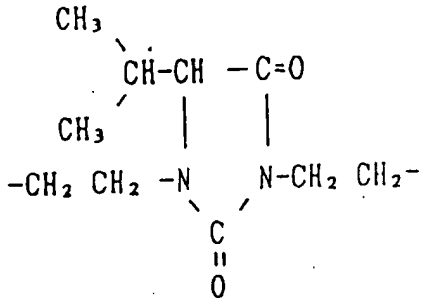
where A is a member selected from the group consisting of an aromatic group, substituted or unsubstituted hydantoin ring, and saturated or unsaturated straight chain hydrocarbon group having 0 - 18 carbon atoms, B is an aromatic group, X which is a substituent attached to B is at least one selected from the group consisting of hydroxy and amino, and Y is a member selected from the group consisting of pyridyl and hydrazino.

Examplary suitable compounds of the formula (I) include compounds (I) where A is an aromatic ring having no substituent other than the hydrazinocarbonyl groups, that is, the following compounds:



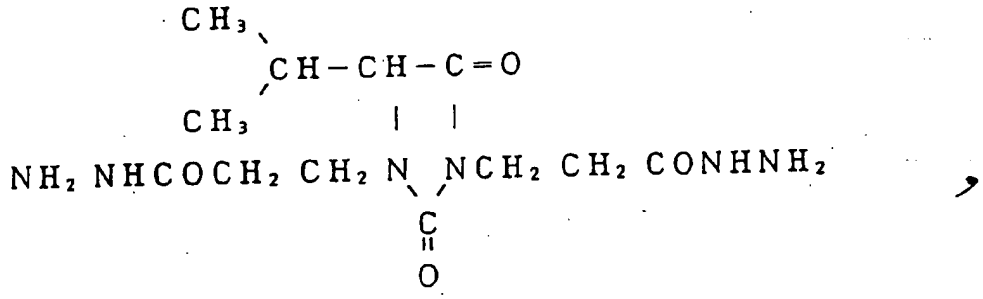
Further exemplary suitable compounds (I) are those having the group A which is a substituted hydantoin ring such as





saturated or unsaturated straight chain hydrocarbon groups having 0 - 18 carbon atoms such as ethylene group, tetramethylene group, heptamethylene group, octamethylene group, octadecamethylene group, 7, 11-octadecadienylene group and the like.

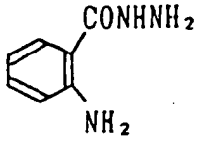
Exemplary suitable compounds of the general formula (I) include phthalic dihydrazide, isophthalic dihydrazide, terephthalic dihydrazide, 1,3-bis(hydrazinocarboethyl)-5-isoprepylhydantoin

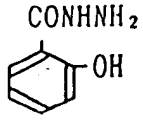


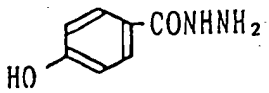
succinic dihydrazide, adipic dihydrazide, azelaic dihydrazide, sebacic dihydride, eicosane dicarboxylic acid dihydrazide, 7,11-octadecadiene-1,18-dicarbohydrazide, and oxalic dihydrazide.

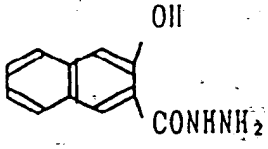
Preferable compound of the formula (II) is that where the aromatic group of B is phenyl or naphthyl and X which is a substituent attached to B is hydroxy or amino.

Exemplary suitable compounds of the formula (II) are:

Anthraniloylhydrazine 

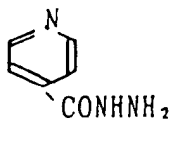
Salicylic hydrazide 

4-Hydroxybenzoic hydrazide 

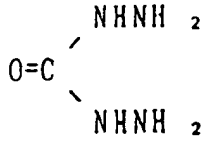
2-Hydroxy-3-naphthoic hydrazide 

Preferable compounds of the formula (III) are that Y is pyridyl or hydrazino.
Exemplary suitable compounds of the formula (III) include

Isonicotinic hydrazide



Carbodihydrazide



The compounds (I), (II) and (III) exhibit excellent heat generation improving effect when they are compounded in rubber.

Rubbers which may be used in the present invention are, for example, natural rubber, synthetic polyisoprene rubber, styrene-butadiene copolymer rubber, polybutadiene rubber, and butyl rubber. These rubbers may be used alone or in combination.

In the present invention, the above-mentioned heat generation improvers may be used alone or in combination. The amount of the heat generation improver to be compounded is 0.05 - 20 parts by weight, preferably 0.1 - 5 parts, more preferably 0.25 - 5 parts.

When the amount of the heat generation improver is less than 0.05 part by weight, the heat generation improving effect can be hardly expected. When the amount exceeds 20 parts by weight, the heat generation improving effect does not increase any more and sometimes mechanical properties of the rubber composition rather decrease.

As the reinforcing filler used in the present invention, there may be mentioned carbon black and the like, and the amount to be used is 20 - 150 parts by weight.

When the amount is less than 20 parts by weight, the rubber composition is not sufficiently reinforced. When the amount exceeds 150 parts by weight, the heat generation characteristics of rubber become worse and in addition, the abrasion resistance and other physical properties are deteriorated.

In the present invention, if necessary, there may be appropriately added to the rubber composition softening agents, antioxidants, vulcanization accelerators, vulcanization accelerating axiliary agents, vulcanizing agents and the like which are additives usually used in rubber industry.

The rubber composition of the present invention may be used for various rubber products such as tires, conveyer belts, hoses and the like.

The invention is now particularly described with reference to the following examples which are for the purpose of illustration only and are intended to imply no limitation thereon.

Examples 1 - 14 and Comparison Example 1

One hundred parts by weight of natural rubber was compounded with 50 parts by weight of ISAF carbon black, 3 parts by weight of stearic acid, one part by weight of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, 5 parts by weight of zinc oxide, one part by weight of N-tert-butyl-2-benzothiazole sulfeneamide, 1.5 parts by weight of sulfur and 1/200 mole of an heat generation improver selected from Table 1 to prepare a rubber composition.

In the same manner, various rubber compositions were prepared using heat generation improvers in Table 1.

The resulting rubber compositions were kneaded with a Banbury mixer and vulcanized to prepare samples. The low heat generation characteristic was evaluated.

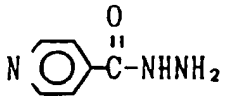
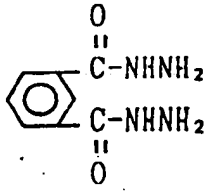
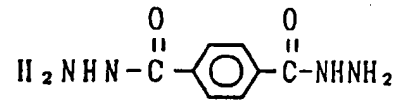
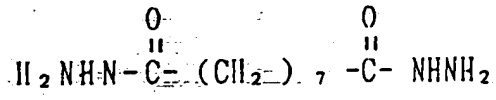
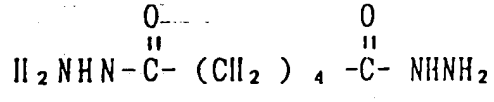
For comparison, a sample prepared by repeating the above-mentioned procedure except that no heat generation improver was added was also evaluated as to the low heat generation characteristic.

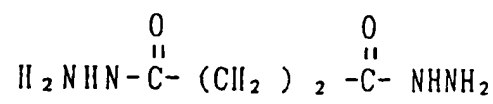
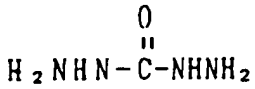
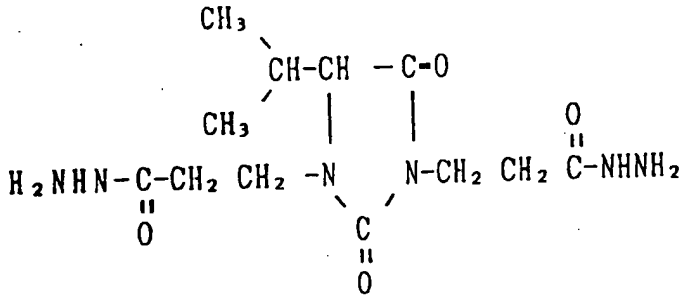
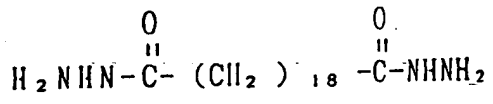
The results are shown in Table 1. The low heat generation index was calculated by the following formula where tan δ was measured at 50°C at a dynamic strain of 5 % with a frequency of 15 Hz by means of a viscoelasticity measuring apparatus manufactured by Rheometric Co.

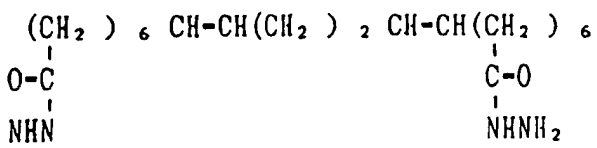
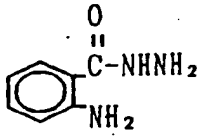
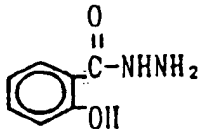
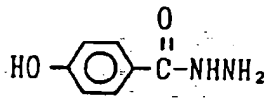
$$\text{Low heat generation index} = \frac{\tan\delta\ (\text{Blank})}{\tan\delta\ (\text{Heat generation improver compounded rubber})} \times 100$$

The larger this index, the less the heat generation.

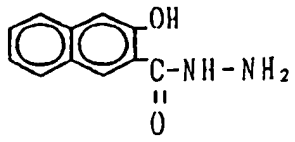
Table 1

| | Heat generation improver | Compounded amount | Low heat generation index |
|---|---|---|---|
| Example 1 | Isonicotinic hydrazide | 0.69 | 114 |
| |  | | |
| Example 2 | Isophthalic dihydrazide | 0.97 | 156 |
| |  | | |
| Example 3 | Terephthalic dihydrazide | 0.97 | 122 |
| |  | | |
| Example 4 | Azelaic dihydrazide | 1.08 | 140 |
| |  | | |
| Example 5 | Adipic dihydrazide | 0.87 | 134 |
| |  | | |

| | Heat generation improver | Compounded amount | Low heat generation index |
|---|---|---|---|
| Exanple 6 | Succinic dihydrizide | 0.73 | 115 |
| |  | | |
| Example 7 | Carbodihydrazide | 0.45 | 113 |
| |  | | |
| Example 8 | 1,3-Bis(hydrazino-carboethyl)-5- iso-propylhydantoin | 1.57 | 142 |
| |  | | |
| Example 9 | Eicosanoic di-carboxylic acid dihydrazide | 1.85 | 126 |
| |  | | |

| | Heat generation improver | Compounded amount | Low heat generation index |
|---|---|---|---|
| Example 10 | 7,11-Octadecadiene-1,18-dicarbohydrazide  | 1.83 | 118 |
| Example 11 | Anthraniloylhydrazine  | 0.76 | 109 |
| Example 12 | Salicylic hydrazide  | 0.76 | 110 |
| Example 13 | 4-Hydroxybenzoic hydrazide  | 0.76 | 107 |

| | Heat generation improver | Compounded amount | Low heat generation index |
|---|---|---|---|
| Example 14 | 2-Hydroxy-3-naphthoic hydrazide | 1.01 | 154 |
| Comparison Example | (Blank) | — | 100 |



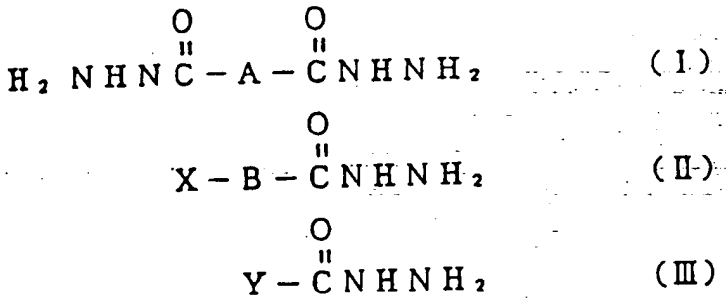
As are clear from the Examples, the rubber heat generation improvers of the present invention exhibit a remarkable heat generation improving effect even when they are incorporated in rubber components such as natural rubber.

Therefore, the rubber composition of the present invention containing a specified amount of the heat generation improver and that of a reinforcing filler exhibits a significantly lowered heat generation without previously modifying the structure of rubber as compared with rubber compositions containing no heat generation improver.

Therefore, the rubber composition having improved heat generation characteristic of the present invention can be easily used in a wide range of technical field and is of a very large value of utilization.

## Claims

1. A rubber composition which comprises 100 parts by weight of at least one rubber selected from natural rubber and diene type synthetic rubbers, 20 - 150 parts by weight of a reinforcing filler, and 0.05 - 20 parts by weight of a compound selected from compounds of the formulas (I) - (III),



(I)

(II)

(III)

where A is a member selected from an aromatic group, substituted or unsubstituted hydantoin rings, and saturated or unsaturated straight chain hydrocarbon groups having up to 18 carbon atoms, B is an aromatic group, X which is a substituent attached to B is at least one of hydroxy and amino, and Y is selected from pyridyl and hydrazino.

2. A rubber composition as claimed in claim 1, characterized by containing 0.1 - 5 parts by weight of the

compound selected from the compounds of the formulas (I) - (III).

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 91 30 8675

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
|---|---|---|---|
| X | GB-A-1 330 393 (SUN OIL COMPANY)<br>* page 2, line 75 - page 2, line 89; claim 1; examples * | 1-2 | C08K5/25<br>C08L21/00 |
| X | GB-A-909 753 (IMPERIAL CHEMICAL INDUSTRIES LIMITED)<br>* page 1, line 26 - page 1, line 33; claim 1; examples * | 1-2 | |
| X | US-A-4 124 750 (J.F.O'MAHONEY,JR.)<br>* column 4, line 61 - column 5, line 4; claim 1; examples * | 1-2 | |
| X | US-A-4 607 060 (C.J.KMIEC ET AL.)<br>* EXAMPLE 8, TABLE VIII, COMPOSITION C * | 1-2 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5) |
| | | | C08K |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 08 JANUARY 1992 | VAN HUMBEECK F. |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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